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EFFECTS OF CONCENTRATION AND OF VIBRATIONAL RELAXATION ON THE INDUCTION PERIOD OF THE $H_2 - O_2$ REACTION

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by F. E. Belles and M. R. Lauver
Lewis Research Center
Cleveland, Ohio

TECHNICAL PREPRINT prepared for Tenth International Symposium on Combustion sponsored by the Combustion Institute and the Cambridge Physical Chemistry Department
Cambridge, England, August 17-21, 1964

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION · WASHINGTON, D.C. · 1964

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Lewis Research Center

SUMMARY

The possibility that slow vibrational relaxation of O_2 or H_2 might affect the induction period of the high-temperature H_2 - O_2 reaction is considered in terms of the data from three different kinds of shock-tube experiments. The data cover a wide range of stoichiometry and temperature and include observations in H_2 - air, H_2 - O_2 - Ar, and H_2 - O_2 mixtures. It is found that induction times in excellent agreement with experiment can be calculated by solving the differential rate equations based on the following simple kinetic scheme: an initiation reaction between molecular species, plus the three usual chain-branching reactions. It is not necessary to invoke vibrational effects to obtain this agreement, but it is necessary to solve the problem without incorporating steady-state assumptions or limitations of stoichiometry. Thus, it is concluded that existing data exhibit little or no effect of slow vibrational relaxation. In support of this conclusion, calculations are presented to show that the greatest possible effect of slow O_2 relaxation would, in fact, be a small one. The calculations were carried out by making the extreme assumption that all the activation energy of the slow chain-branching step must be supplied by vibrational energy of O_2. Since the level of this energy varies during the induction period in a

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manner governed by the vibrational relaxation time, the reaction rate constant becomes time dependent. Unfortunately, the equivalent calculations for H_2 cannot be made, because the relaxation time of H_2 in the presence of O_2 is not known.

INTRODUCTION

If a gaseous mixture containing hydrogen and oxygen is suddenly heated to a temperature greater than about 1000° K at moderate pressure, for example, by means of a shock wave, its ignition is preceeded by a short induction period. During this interval, chain branching occurs, and since the induction period comes before the heat-releasing part of the reaction, the chain-branching process takes place under conditions of essentially constant temperature and pressure. Moreover, the time is so short - a few to a few hundred microseconds - that wall effects cannot make themselves felt.

Thus, measurements of the induction period permit the chain-branching process to be studied in a relatively uncomplicated environment. This fact was perhaps first recognized by Schott and Kinsey[1], who made an extensive set of measurements over a wide range of temperature and $[H_2]/[O_2]$ ratios from 0.25 to 5.

Only four reactions are needed to describe the buildup of free radicals during the induction period. First, there must be an initiation reaction involving molecular species. In the lower range of temperatures (1000° - 2000° K) this may be the following[2]:

$$H_2 + O_2 \rightarrow 2OH \qquad \text{(i)}$$

After a short initiation period, which calculations show will occupy only a small part of the total induction period[2], the following reactions branch the chain:

$$OH + H_2 \rightarrow H_2O + H \qquad (I)$$

$$H + O_2 \rightarrow OH + O \qquad (II)$$

$$O + H_2 \rightarrow OH + H \qquad (III)$$

Rate constants are available for all of these reactions[2,3].

Schott and Kinsey correlated their data by plotting the parameter $t_i[O_2]$ against reciprocal temperature. They took the induction period t_i, which of course must always be defined somewhat arbitrarily, as the time at which [OH] reached the limit of detectability in their experiments, about 10^{-6} mole/liter. They noted that this correlation is the one to be expected if chain branching is controlled by the rate of the slow step, reaction (II).

However, they observed a trend in their data such that $t_i[O_2]$ increased with increasing mole fraction of oxygen at constant temperature. This is not anticipated on the basis of the simplified kinetic model in which the controlling rate is that of reaction (II). Schott and Kinsey tentatively ascribed this trend to slow vibrational relaxation of oxygen, which might tend to reduce the rate of reaction (II) below the value it would have under conditions of full thermal equilibrium. This amounts to the suggestion that at least part of the activation energy normally resides in vibrations of the oxygen molecule.

In order to investigate this important possibility more fully, it is necessary to consider data for the widest possible range of $[H_2]/[O_2]$ ratios (and hence, of relaxation times); the data of White and Moore[4] are extremely valuable on this account. If the data are to be interpreted in the light of reactions (i) to (III), then it is also important not to suppress any implications of this kinetic scheme; that is, the differential rate equations must be solved without incorporating any assumptions about steady states or stoichiometry. If, after this, any discrepancies remain, they can be discussed in terms of slow vibrational relaxation.

EFFECTS OF CONCENTRATION ON INDUCTION PERIOD

Calculations

In order to calculate the concentration of H, O, or OH as a function of time during the induction period, it is necessary to integrate the set of differential equations based on reactions (i) to (III). An obvious way to solve the problem without making any simplifying assumptions is by numerical integration, carried out with the aid of a high-speed computing machine. Such numerical integrations have been reported[5] for 5-percent-H_2 - 95-percent-air mixture, and they were used to explain the chemiluminescence of hydroxyl radical during the induction period. These calculations showed that after a brief initiation period the free-radical concentrations adopt the following simple time dependence:

$$\frac{[H]}{[H]_0} = \frac{[O]}{[O]_0} = \frac{[OH]}{[OH]_0} = \exp\left(\frac{t}{\tau}\right) \tag{1}$$

The quantities with subscript 0 are pseudoinitial concentrations, obtained by extrapolating the linear part of a semilogarithmic plot to time zero.

The simple form of Eq. (1) strongly suggests that there is a general analytic solution for the induction-period kinetics. This is actually the case, and it is due to the fact that reactions (I) to (III) are in effect first-order reactions because $[O_2]$ and $[H_2]$ remain constant during the induction period. The method of solution for such situations is outlined in standard text books[6], and the solution was carried out by Kondratiev[7] for the kinetic scheme used in the present paper. Nicholls, Adamson, and Morrison[8] also appreciated the inherent simplicity of the induction-zone kinetics, but they dealt with a more extensive set of reactions and introduced approximations which lead to a solution good only if $[H_2]$ and $[O_2]$ are of order unity. Therefore, their solution is not adequate to deal with a very large range of $[H_2]/[O_2]$ ratios.

Brokaw[9] has recently presented an approximate technique by means of which an analytic solution can be obtained that gives excellent agreement with the results of numerical integration of the induction-zone kinetics. He obtains the following expressions which are applicable to the high-temperature regime of short induction times:

$$\frac{1}{\tau} = [H_2]\left\{\frac{2k_1k_3\left[\left(1 + \frac{8k_2[O_2]}{k_3[H_2]}\right)^{1/2} - 1\right]}{2 + \left(1 + \frac{k_1[H_2]}{k_2[O_2]}\right)\left[\left(1 + \frac{8k_2[O_2]}{k_3[H_2]}\right)^{1/2} + 1\right]}\right\}^{1/2} \tag{2}$$

and

$$[OH]_0 = \frac{2k_i[O_2]}{k_1} \tag{3}$$

Equation (3) expresses the reasonable notion that the initiation reaction will cease to be important when the fastest chain-branching reaction (I) uses up OH as rapidly as it is produced by the initiation reaction.

From the previous results the induction time of Schott and Kinsey[1] ($[OH] = 10^{-6}$ mole/l), multiplied by the oxygen concentration, can immediately be written as

$$t_i[O_2] = \frac{[O_2]}{[H_2]}\left\{\frac{2 + \left(1+\frac{k_1[H_2]}{k_2[O_2]}\right)\left[\left(1+\frac{8k_2[O_2]}{k_3[H_2]}\right)^{1/2} + 1\right]}{2k_1k_3\left[\left(1+\frac{8k_2[O_2]}{k_3[H_2]}\right)^{1/2} - 1\right]}\right\}^{1/2} \ln\left[\frac{10^{-6}}{2k_i[O_2]/k_1}\right] \quad (4)$$

There are two main points to be made about Eq. (4). The first is that the parameter $t_i[O_2]$ should not succeed in correlating induction times obtained over a wide range of $[H_2]/[O_2]$ ratios. The second is that the effect of the initiation reaction is small, since it is in the logarithmic term; thus, a large error could be made in $[OH]_0$ without materially affecting the result calculated from Eq. (4). This is fortunate, because there is no independent evidence as to the rate constant or even the occurrence of reaction (i).

We shall also want to compare calculated induction times with experimental values obtained by two other techniques. The most important set of data is due to White and Moore[4], who measured the period of constant density behind shock waves by interferometry. In a preliminary report[10], White noted that the times obtained in this way are similar to those reported by Schott and Kinsey. It will therefore be assumed that the two kinds of measurements are essentially equivalent, and Eq. (4) will also be used for comparisons with White and Moore's results.

Finally, a limited amount of new data will be presented, which was obtained from observations of light emitted at 3080 Å by electronically excited hydroxyl radical OH^*. The interpretation[5] of this light predicts an inflection point in the curve of light intensity against time behind the shock front, due to competition between the reaction producing the excited molecule,

$$H + O_2 + H_2 \rightarrow H_2O + OH^* \qquad (IV)$$

and collisional quenching by water produced in reaction (I),

$$OH^* + H_2O \rightarrow OH + H_2O \qquad (V)$$

The inflection time is given by the following expression[5]:

$$t_{inflection} = \tau \ln\left[\frac{(1/\tau)^2}{k_1 k_5 [H_2][OH]_0}\right] \qquad (5)$$

The quantities $(1/\tau)$ and $[OH]_0$ may be obtained by means of Eqs. (2) and (3). The rate constant k_5 is taken as the binary collision number.

The other rate constants used for calculations are listed in Table I. They are either literature values or are adjusted, with literature values as a starting point, as described in the footnote of Table I. In effect, all comparisons between calculated and observed induction times have been normalized to one particular set of experimental data by means of the tabulated set of rate constants. However, it should not be inferred that this set is unique, or that it represents improved absolute values.

Comparison with Experiment

Light-emission experiments. - Inflection times were measured from oscilloscope records of light intensity behind shock waves traveling through 5- and 20-percent H_2 - air mixtures at 10 Torr initial pressure.

Zero time was fixed by arrival of the shock at a thin-film resistance gauge, located at the same axial position as the slit through which emitted light was transmitted to a monochromator and photomultiplier detector. Details of the experiment are given in Ref. 5, which also includes the data for the 5-percent mixture.

Results are plotted in Fig. 1, which also shows inflection times calculated from Eq. (5) as solid lines. The temperatures used to plot the data were calculated from shock velocity by the graphical method of Markstein[11], and they represent full thermal equilibrium behind the shock.

Since the rate constants were chosen for a good fit to the 5-percent data at intermediate temperatures, the upper solid line naturally agrees well with the experimental results. Inflection times for the 20-percent mixture are predicted to be about half as great at a given temperature. Despite a higher degree of scatter, due largely to the fact that shock velocities were not as uniform as in the leaner mixture, the 20-percent data bear out this prediction quite well.

It was pointed out in the earlier work[5] that Eq. (5) is derived from an approximation which becomes worse as the temperature increases. In order to assess this effect, the differential equations based on reactions (i) to (V) were integrated numerically to give [OH*] as a function of time, and inflection times were obtained from the plotted results. These more accurate times were only 10-percent larger at the highest temperature considered (1900° K), so Eq. (5) is indeed a very good approximation.

The simplifying kinetic assumptions adopted by Schott and Kinsey[1] and by Nicholls, Adamson, and Morrison[8] lead to the conclusion that $(1/\tau)$ should be given by the following expression:

$$1/\tau \simeq 2k_2[O_2] \tag{6}$$

This result, when inserted in Eq. (1), provides the basis on which Schott and Kinsey expected their data to correlate in terms of the parameter $t_i[O_2]$. It can be seen from Eq. (5) that the same correlation should hold for the light-emission data of Fig. 1, if Eq. (6) were correct; but $[O_2]$ is only about 1.2 times as large in the 5-percent as in the 20-percent mixture, while the data differ by a larger factor, so the correlation will not bring the results together.

<u>Light-absorption experiments.</u> - Although the work of Schott and Kinsey covered a much wider range of $[H_2]/[O_2]$ ratios than the light-emission studies just discussed, the failure of the $t_i[O_2]$ correlation was obscured by scatter in their results. However, they did observe that when the data for each mixture was considered separately, $t_i[O_2]$ varied with mole fraction of oxygen. The values they obtained, for a constant induction-zone temperature of 1800° K, are quoted in the last column of Table II. Each mixture is designated by a letter as in the original work[1].

The first two columns of calculated results give values obtained by means of Eq. (4) and by numerical integration. There is no more than 10-percent difference in any of the pairs of numbers, so it can be concluded that Eq. (4) is valid over the full range of $[H_2]/[O_2]$ ratios.

Comparison of either column of calculations (constant k_2) with the experimental results is very gratifying. The worst discrepancy is a factor of about 2 for mixture A. Thus, simple calculations based on reactions (i) to (III) can explain the results of the light-absorption experiments quite well without invoking effects due to slow vibrational relaxation.

Interferometric experiments. - The induction-period measurements of White and Moore[4] cover an extremely wide range of $[H_2]/[O_2]$ ratios (0.0075 to 24), so they provide the best test of the simple kinetic scheme adopted in the present paper. In Fig. 2, their data are reproduced, together with lines calculated for eight of the nine $[H_2]/[O_2]$ ratios studied. The calculations were made by means of Eq. (4), assuming a constant induction-zone pressure of 1 atmosphere in all cases. Inasmuch as the pressure only enters via $[O_2]$, in the logarithmic term of Eq. (4), the result is quite insensitive to the assumed pressure, and moreover White[12] has stated that 1 atmosphere is a reasonable average for these experiments.

Inspection of Fig. 2 shows that experiment and calculation agree very well indeed. At a given temperature, the parameter $t_i[O_2]$ decreases as the $[H_2]/[O_2]$ ratio increases, spanning nearly two orders of magnitude from the leanest to the richest mixture. The major discrepancy seems to be in the richest mixtures, where calculations for $[H_2]/[O_2]$ ratios of 7 and 24 give two lines quite close together, whereas the data for these two mixtures appear to be more widely separated. However, it must be borne in mind that the calculated t_i corresponds to the time at which $[OH] = 10^{-6}$ mole/liter, and there is no real assurance that

White and Moore's data should coincide, since they are based on density changes rather than concentration of OH. In any event, the discrepancies between experiment and calculation are no more than a factor of two at worst.

The slopes of the calculated lines undergo a noticeable increase as $[H_2]/[O_2]$ ratio increases, with a rather marked change taking place between $[H_2]/[O_2]$ ratios of 0.10 and 0.33. This behavior is due to the increased importance of reaction (III), with its smaller activation energy, in the leaner mixtures, while in those less abundantly supplied with O_2, reaction (II) assumes more control.

White and Moore observed[4] that their data can be correlated if the parameter $t_i([O_2][H_2])^{1/2}$ is used instead of $t_i[O_2]$. It is not readily apparent that Eq. (4) can predict this correlation. It does follow, however, if one considers a less exact solution of the induction-zone kinetics. Brokaw[9] found that a rather good first approximation to $(1/\tau)$ can be obtained by imposing a steady state on OH (but not on O and H):

$$\frac{1}{\tau} \simeq \frac{k_3[H_2]}{2} \left[\left(1 + \frac{8k_2[O_2]}{k_3[H_2]}\right)^{1/2} - 1\right] \qquad (6)$$

The approximate time at which $[OH] = 10^{-6}$ mole/liter is therefore

$$t_i \simeq \frac{2}{k_3[H_2]} \left[\left(1 + \frac{8k_2[O_2]}{k_3[H_2]}\right)^{1/2} - 1\right]^{-1} \ln\left[\frac{10^{-6}}{2k_i[O_2]/k_1}\right] \qquad (7)$$

Equation (7) shows that the parameter $t_i([O_2][H_2])^{1/2}$ will approximately correlate the data provided that

(a) $$\ln \frac{10^{-6}}{2k_i[O_2]/k_1} \simeq \text{constant}$$

(b) $$\left(1 + \frac{8k_2[O_2]}{k_3[H_2]}\right)^{1/2} \gg 1$$

At any given temperature in the experimental range, calculation shows that criterion (a) is well satisfied for all $[H_2]/[O_2]$ ratios studied by White and Moore and that (b) holds very well for the leaner mixtures up to $[H_2]/[O_2] = 0.33$. Consequently, a plot of $t_i([O_2][H_2])^{1/2}$ as a function of $1/T$ should, at the very least, bring together the data for all the lean mixtures, so the correlation does have a basis in the induction-zone kinetics.

DISCUSSION

The foregoing comparisons between calculated and observed induction times show that the experimental results are explained by straightforward application of a simple kinetic scheme. There is no need to invoke effects due to slow vibrational relaxation of O_2 or H_2.

Perhaps this is not a surprising result, because there is no a priori reason to believe that reactions (i) to (III) normally obtain part of their activation energy from internal degrees of freedom. On the other hand, many reactions do. The measured rates of thermal dissociation of simple molecules, for example, usually have to be interpreted by assuming that internal energy contributes[13]. Of course, such dissociation reactions are strikingly different from those occurring in the induction period of the H_2 - O_2 reaction, but it is nevertheless worthwhile to see if calculations can confirm that vibrational effects should be absent, or at least small.

First of all, it must be acknowledged that some or all of the initiation process, whether by reaction (i) or some other reaction, will proceed in vibrationally cold gas. But Eqs. (4) and (5) show that induction time is extremely insensitive to the rate of initiation; therefore, it is unlikely that experiment could detect vibrational effects here.

Of the much more important reactions, namely, those that branch the chain, only reaction (II) involves the oxygen molecule. Therefore, let us next consider what would happen to the induction time if the vibrational energy of O_2 were needed for activation. The simplest way to compute an upper limit for the effect is to assume that all the activation energy must reside in vibrations. In other words, RT is replaced by RT_v, where T is the overall temperature of the induction zone and T_v is the vibrational temperature of O_2 at a given instant, yielding

$$k_2 = A_2 \exp(-E_2/RT_v) \tag{8}$$

The timewise history of T_v, starting from 300° K, may be written as follows[14]:

$$T_v = T - (T - 300)\exp(-t/t_v) \tag{9}$$

where t_v is the vibrational relaxation time.

White and Millikan have presented data[15-17] and a general correlation[18] that permit the relaxation time of O_2 in any mixture containing

O_2, H_2, Ar, and N_2 to be estimated. Values calculated at 1800° K for the $H_2 - O_2$ - Ar mixtures used by Schott and Kinsey[1] are listed in column 5 of Table II. These times differ considerably from those estimated by Schott and Kinsey, due to the subsequent discovery[17] that H_2 is extremely effective in collisionally exciting the O_2 vibrations. The range of ratios of observed t_i to t_v is 2.6 (mixture H') to 16.9 (mixture D), so the time required for relaxation is always less than the measured induction times.

The differential rate equations containing the time-dependent k_2 (Eqs. (8) and (9)) were integrated by means of a high-speed machine program. The time at which [OH] = 10^{-6} mole/liter was read off from the plotted results. Figure 3 contrasts the behavior when k_2 is constant and when it is a time-varying function of the O_2 vibrational temperature in mixture H', the one for which t_v comes closest to t_i. Remarkably, the extreme assumption that all the activation energy must come from vibrational energy of O_2 only increases t_i by 20 percent. Similarly small effects for the other mixtures are shown in Table II.

The slightly more difficult integration based on reactions (i) to (V) was also carried out subject to a time-varying k_2 so that inflection times could be obtained for comparison with the light-emission experiments in 5- and 20-percent H_2 - air mixtures. The results are plotted as dashed lines in Fig. 1.

At this point it is necessary to decide whether the data points in Fig. 1 can be compared with the dashed lines. It will be recalled that the points represent observed inflection times plotted against the reciprocal of the full-thermal-equilibrium temperature, as calculated from shock speed by Markstein's method[11]. But there is actually a marked temperature variation in the induction zone, because these mixtures contain quite a lot of O_2 to absorb energy in vibrations. For example, if the thermal-equilibrium temperature of the induction zone in 20-percent H_2 - air mixture is 1900° K, the temperature just behind the shock will be about 2070° K. In contrast, the mixtures used by Schott and Kinsey were (except for H) heavily diluted with argon, so the process of vibration relaxation had little effect on the overall induction-zone temperature.

However, calculation of the vibrational relaxation times for O_2 in the H_2 - air mixtures shows that the process is very fast, because of the appreciable mole fraction of H_2 present. At 1500° K, for instance, the observed inflection times are about 6 times longer than the calculated relaxation times in the 5-percent mixture, and in the 20-percent mixture, about 10 times longer. Therefore, the temperature of the induction zone during most of its history will be close to the full-thermal-equilibrium value, and it is indeed appropriate to use that temperature in plotting the data.

Returning now to Fig. 1, it is seen that the points for higher temperatures perhaps come closer to the dashed lines calculated for the case of slow O_2 relaxation. However, the predicted effects are again small, just as in the mixtures studied by Schott and Kinsey, and the data are certainly not good enough to warrant any positive conclusion.

It is more difficult to consider what might happen if slow vibrational relaxation of H_2 played a role in the chain-branching kinetics. In the first place, H_2 participates in two of the reactions (I and III), and it is best to consider only one at a time for the sake of clarity; but more important is the fact that the vibrational relaxation time of H_2 in H_2 - O_2 mixtures is unknown.

If relaxation is assumed to occur by a simple collision process, the time can be calculated[18], and it turns out to be extraordinarily long due to the very high characteristic temperature of the molecule. In fact, the collisional relaxation times turn out to be much longer than observed induction periods. However, White and Moore[4] have found that the process is greatly accelerated by exchange of vibrational energy from O_2, the more rapidly relaxed component; in fact, it is so fast that it cannot be resolved interferometrically in their experiments. Therefore, values of t_v for H_2 in the presence of O_2 are unavailable at present, and it is not possible to carry out calculations in which Eq. (9) is used to make k_1 or k_3 time-dependent. But reasoning by simple analogy from the results obtained with a time-dependent k_2, it certainly seems likely that the effect of H_2 relaxation on induction time would be small.

CONCLUSIONS

The following conclusions are drawn from this work:

(1) Induction times for the hydrogen-oxygen reaction, measured behind shock waves by various techniques and over a very wide range of $[H_2]/[O_2]$ ratios, can be explained by a simple kinetic scheme consisting of an initiation reaction and the usual three chain-branching reactions.

(2) Calculated induction times based on this scheme are in excellent agreement with experiment when reasonable values for the rate constants are used.

(3) This agreement, in the case of H_2 - air mixtures, indicates that N_2 does not play a significant part in the induction-period kinetics. While perhaps not unexpected, this fact is pertinent to practical considerations of air-breathing hydrogen-fueled engines.

(4) Calculations based on extreme assumptions about the possible role of vibrational energy in the chain-branching reactions show that slow relaxation of O_2 could have only a small effect on induction time, probably not detectable experimentally. Equally confident statements cannot be made about the possible results of slow relaxation of H_2, because its relaxation time in H_2 - O_2 mixtures is unknown; however, it is very likely that this effect (if it exists) is also a small one.

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TABLE I. - RATE CONSTANTS, $k = A \exp(-E/RT)$

Reaction	A, l/mole-sec	E, cal/mole	Source of data
i	1.0×10^{11}	70,000	Ref. 2
I	6.3×10^{10}	5,900	Ref. 3
II	4.0×10^{11}	17,000	Adjusted[a]
III	1.2×10^{10}	8.950	Adjusted[a]

[a]Adjusted to give good fit to light-emission data obtained for 5-percent-H_2 - 95-percent-air mixture over the temperature range from about 1200° to 1600° K. These k's represent increases in the values given by Baldwin[3] for k_2 and by Kaufman and Del Greco[3] for k_3. The maximum change is a factor of 1.8 times Baldwin's k_2 ($2.0\times10^{11} \exp(-16{,}600/RT)$) and 3.4 times Kaufman and Del Greco's k_3 ($2.5\times10^{9} \exp(-7700/RT)$).

TABLE II. - COMPARISON OF CALCULATED AND OBSERVED VALUES OF $t_1[O_2]$ AT 1800° K

1	2	3	4	5	6			
Mixture	O_2, percent	$[H_2]/[O_2]$	$^a[O_2]$, (mole/l) $\times 10^5$	t_v, sec $\times 10^6$	$t_1[O_2]$, sec(mole/l) $\times 10^9$			
					Calculated			Observed
					Constant k_2		Time-dependent, k_2	
					Eq. (4)	Numerical		
A	0.43	1.6	2.5	16.2	5.7	5.7	6.1	2.7
B	.49	2.0	2.6	15.1	5.1	5.4	5.7	3.7
D	.45	5.5	4.0	4.6	3.3	3.6	3.8	3.1
F	.49	2.0	12.0	3.2	4.5	4.6	4.9	4.5
C	1.99	1.9	12.0	4.0	4.6	4.7	5.2	4.7
E	2.00	.5	21.0	7.3	8.9	9.2	10.7	5.4
H'	4.00	.25	37.0	8.1	13.5	13.8	16.5	7.8
H	19.7	.25	49.0	7.7	13.2	13.7	17.4	11.7

[a] G. L. Schott, private communication, Dec. 1963.

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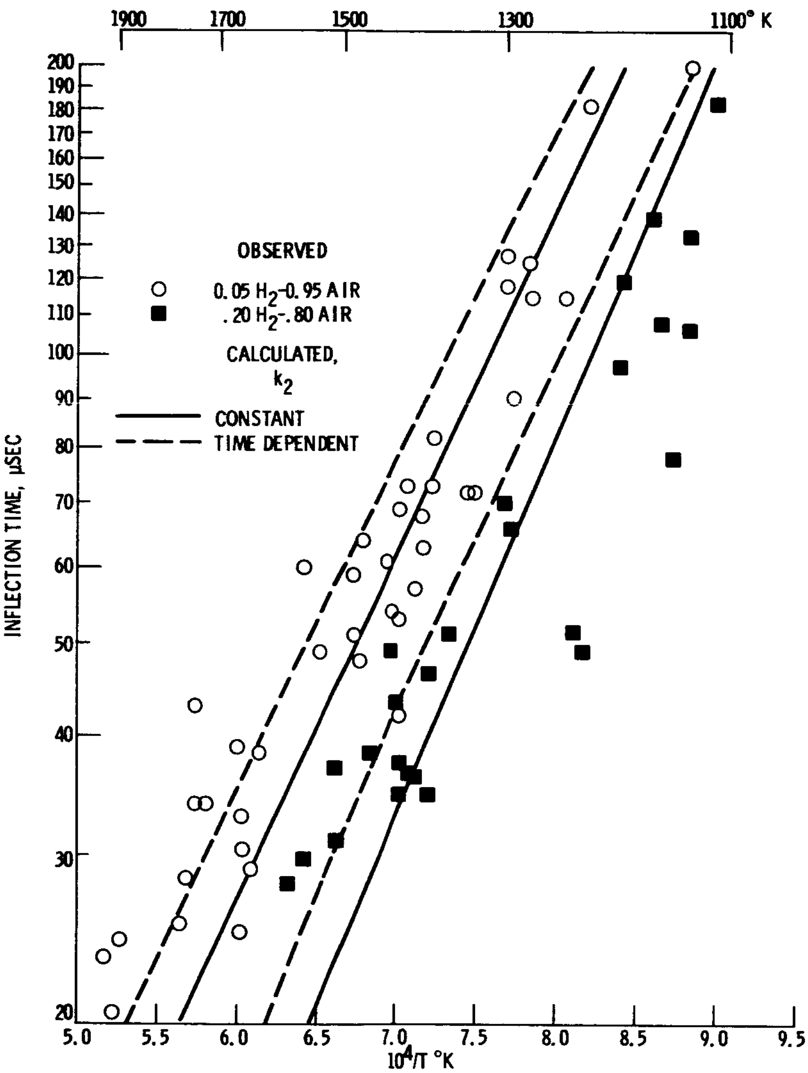

FIG. 1. - COMPARISON OF CALCULATED AND OBSERVED TIMES OF INFLECTION IN RECORDS OF $OH^{*}\ {}^2\Sigma^+ \rightarrow {}^2\Pi$ EMISSION INTENSITY AS FUNCTION OF TIME.

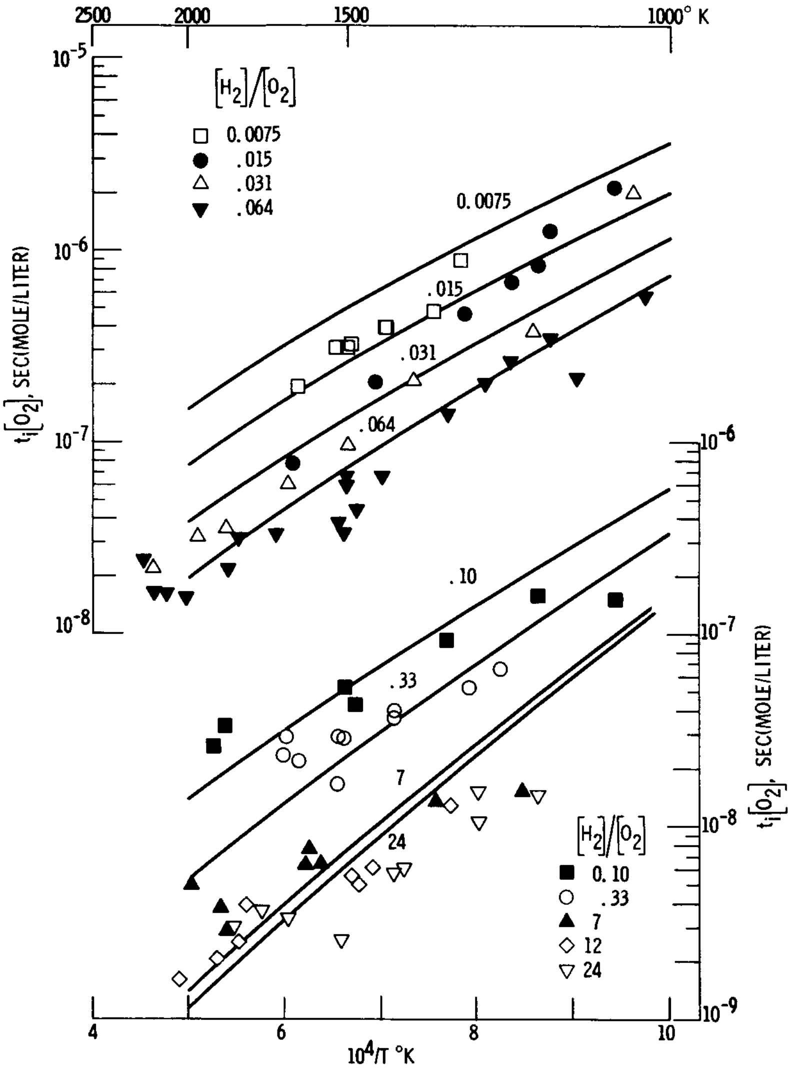

FIG. 2. - COMPARISON OF CALCULATED INDUCTION TIMES WITH EXPERIMENTAL DATA OF WHITE AND MOORE.

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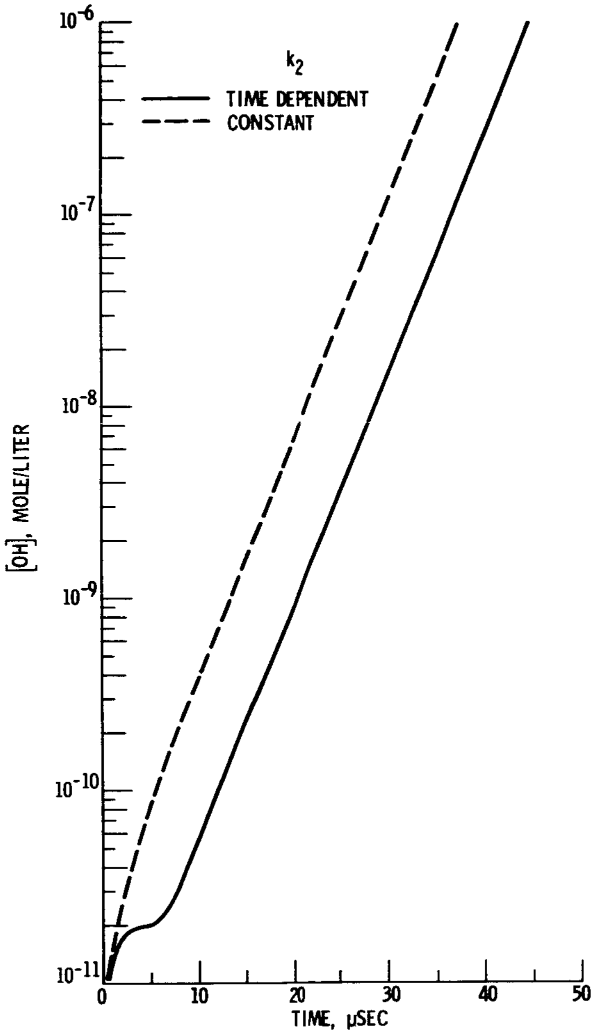

FIG. 3. - EFFECT OF TIME-DEPENDENT k_2 ON OH CONCENTRATION DURING THE INDUCTION PERIOD IN 0.01 H_2 - 0.04 O_2 - 0.95 Ar MIXTURE AT 1800° K.